Layered Nano Composites - Interface characterization of Fe/AlN multilayered film

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Four kinds of Fe/AlN multilayered thin films were deposited by rf-sputter deposition at room temperature. Both Fe and AlN layers have almost the same thickness and their total film thickness was about $1\mu\text{m}$. They have stacking sequences of 1, 3, 8 and 35, respectively. They showed an anisotropic magnetic behavior; soft ferromagnetic along the film surface and mostly paramagnetic in the vertical direction. Formation of both iron nitride and aluminum metal were detected at their interface by XAFS, Mössbauer spectroscopy and XPS even though the films were prepared at room temperature.

Keywords: nanocomposite, Fe/AlN, multilayer, interface, magnetic behavior, radio frequency sputter deposition, Mössbauer, X-ray absorption fine structure, X-ray photoelectron spectroscopy

I. Introduction

Electrical properties in stacked layered crystal structure are affected by interactions between the layered structural units. Size matching was important between CuO_2 conduction plane and modifying layer in oxide superconductors for their effective carrier doping. Oxygen nonstoichiometry occurred to reduce the stress in the respective layered structural units caused by a slight size difference in the stacked layered structure⁽¹⁾. Sulfur deficiency was found out in rocksalt type LaS layer sandwiched with VS_2 layers in a misfit layered compound $(\text{LaS})_{1.18}\text{VS}_2$ ⁽²⁾ although gadolinium defect had been reported in a similar misfit layered $(\text{GdS})_{1.27}\text{CrS}_2$ ⁽³⁾. These nonstoichiometries in LnS layer could also be understood from the tendency to reduce the stress induced from size difference in layered structural units in the misfit layered compounds. These are examples of interface interaction in multilayers at crystal structural level.

Grain boundary and interface plays important roles in ceramics in spite of their small volume fraction against total body. Their analysis and understanding are still in a preliminary stage.

It is important to develop methods of both their sampling and analyses for their science and applications. Stacked layered composites especially multilayers have a large fraction of two dimensional interface against total sample body. It can be expected that three dimensional periodical atomic arrangements have been severely disturbed at the interface region between solids. Diffraction method may be useless for their analyses. Spectroscopy such as XAFS, XPS and Mössbauer may be effective. Reflection spectroscopies are very useful for the film samples deposited on substrate.

Iron nitrides are attractive materials for magnetic applications because of both their large saturation magnetization B_s and small coercivity H_c ⁽⁴⁾. They are thermally unstable to release nitrogen by their heating up to several hundred °C. Addition of other elements such as Zr, Ti etc has been investigated to improve their thermal instability. Increase of thermal stability was expected because these elements themselves form thermally stable metallic nitrides with rocksalt type structure. Covalent nitrides, Si_3N_4 and AlN, are high temperature ceramics. Iron metal fine particles had been precipitated by an annealing of co-

sputter deposited M-Fe-N (M=Al, Si) films⁽⁵⁾. We are also interested in layered composites of Fe with these covalent nitrides. Magnetic and magneto-optical study has been reported on Fe/AlN multilayers⁽⁶⁾. Their coercivity showed a broad minimum of 4 to 5 Oe in the Fe layer thickness range of 6 to 10nm and a slight increase of Faraday rotation was also observed at around 4nm thickness. However neither their structure nor the interface have not yet been investigated in the previous study.

In the present investigation, we prepared four kinds of Fe/AlN multilayers by rf-sputtering, and performed their structure and interface characterization as well as magnetic investigation.

II. Experimental

Multilayered films were prepared on glass slide or silica glass substrates with rf-sputter deposition equipment JEOL JEH-430RS without substrate heating. AlN was deposited at a rate of 0.31nm/s with Al target (4N grade, Kojundo Chemical Laboratory Co., Ltd) using 6N nitrogen as a sputter gas. Fe layer was precipitated at a rate of 0.32nm/s with Fe target (4N grade, Kojundo Chemical Laboratory Co., Ltd) using 6N argon as a sputter gas. They were sequentially deposited under the constant deposition rates. The sputter gas pressure was kept at 1Pa and the applied rf-power was 30W for each layer deposition. The deposition chamber was evacuated down to a base pressure below 1×10^{-4} Pa at the deposition intervals. Each layer thickness was changed with their deposition duration. We obtained four kinds of multilayered composite film represented in Table 1. The multilayered depositions were confirmed by RBS. It was not possible on the film (d) because of its resolution limit. Magnetic behavior was investigated by BH tracer in a magnetic field below 8 Oe.

III. Results & discussion

X-Ray diffraction showed only α -Fe 110 diffraction lines as shown in Fig.1. AlN was deposited as amorphous and α -Fe was strongly preferred oriented to [110]. Superlattice diffractions due to the deposited layer sequence were also observed around $2\theta = 5^\circ$ only on the film (d). Broad halos between $2\theta = 20^\circ$ and 30° were due to the substrate glasses. The 110 diffraction line became broader and shifted gradually to lower angle from the film (a) to (d). The cubic lattice parameters were 0.2894, 0.2896, 0.2898, 0.2923nm, and the crystallite sizes estimated by the line broadening were 8.3, 7.9, 7.0, 2.7nm for the films (a) to (d), respectively. The lattice parameter expanded from the value $a = 0.28664$ nm for bulk α -Fe (JCPDS 6-696) and the crystallite size became smaller with a decrease of single layer thickness. The degraded crystallite size can be understood in relation to the decreasing layer thickness. The expansion of α -Fe crystal lattice was originally assumed to be related to a difference of thermal expansion between α -Fe ($\beta > 1 \times 10^{-5} \text{K}^{-1}$) and AlN ($\beta < 1 \times 10^{-5} \text{K}^{-1}$).

Very anisotropic magnetic behavior was observed on the multilayers. Figure 2 shows a case of film (d). Coercivity H_c was small under a magnetic field applied parallel to the film surface in spite of its small α -Fe crystallite size of a single domain level. Saturation magnetization B_s was around 10kG because the volume fraction of α -Fe was about a half of the total film. Mostly paramagnetic behavior was observed with a small amount of ferromagnetic component under a magnetic field applied perpendicular to the film surface. Coercivity of the ferromagnetic contribution in the latter gradually increased with a decrease of single α -Fe layer thickness: 30 Oe for film (a), 34 Oe for film (b), 47 Oe for film (c) and 53 Oe for film (d).

Table 1 Multilayered Fe/AlN film*

Film	Periodicity	Fe single layer thickness/nm	AlN single layer thickness/nm	Total thickness / μm
(a)	1	495.7	434.3	0.93
(b)	3	178.2	169.4	1.04
(c)	8	64.8	61.6	1.01
(d)	35	6.5	6.2	0.44

* Top layers were AlN thin films to prevent from Fe oxidation.

Fig. 1 X-ray diffractions for multilayered Fe/AlN films.

Fig. 2 B-H curve of multilayered Fe/AlN film (d) under magnetic fields applied parallel and vertical directions against the film surface.

Magnetic moment in the [110] preferred oriented single α -Fe layer became more difficult to rotate to a direction along a $\langle 100 \rangle$ easy axis in the thinner layer.

X-Ray absorption spectroscopy for Fe K-edge revealed unexpectedly interesting nature of the interface. It was measured by He ion yield XAFS. Samples (b) and (d) gave the spectra depicted in Figs. 3(B) and (C). The spectrum (B) resembles to the bulk α -Fe film spectrum (A). The spectrum (C) shows similarities for the both spectra (D) and (E) rather than those for (A) and (B). The pre-edge around 7.11keV can be assigned to $s \rightarrow d$ quadrupole transition of tetrahedrally coordinated iron. $\text{FeN}_{0.91}$ had been prepared by rf-sputter deposition and assumed to have a zinc blende-type crystal structure⁽⁷⁾. Its spectrum

Fig. 3 Fe K-edge X-ray absorption spectra XAFS.

Fig. 4 Fourier transform of EXAFS for multilayered Fe/AlN film (d).

in Fig. 3(E) clearly shows this pre-edge. Tetrahedrally coordinated Fe with four nitrogen atoms are present in the multilayered film (d) $[\text{Fe}(6.5\text{nm})/\text{AlN}(6.2\text{nm})]_{35}$ as well as in a 60% Fe dispersed Fe-Al-N amorphous film as expected from the spectra (C) and (D). It was also con-

Table 2 Resultant EXAFS parameters

Samples	Scatter	r/nm	CN	σ^2/pm^2	Scatter	r/nm	CN	σ^2/pm^2
FeNo. ₉₁	N	0.188	4.0	38.7	Fe*	0.306	4.0	
film (d)	N	0.189	3.2	86.2	Fe	0.244	5.0	133
film (b)	Fe	0.247	7.9	56.0				
Fe*	Fe	0.248	8.0		Fe	0.287	6.0	
Fe ₃ Al*	Fe	0.250	8.0		Al	0.289	6.0	

* Values from the crystal structure.

firmed by Fourier transform of Fe K-edge EXAFS oscillation⁽⁸⁾. The film (d) shows strong distribution intensities at 0.19nm and at 0.25nm as depicted in Fig. 4. The former distance corresponds to the nearest neighboring Fe-N bond distance in FeNo.₉₁. The latter value is almost the same with the nearest neighboring Fe-Fe distances both in α -Fe and in Fe₃Al as represented in Table 2. However only the distribution intensity for Fe was observed on the film (b).

Mössbauer spectrum for film (a) shows only preferred oriented α -Fe as depicted in Fig. 5. The spectrum gradually became more complicated from the film (a) to (d) with the decrease of single layer thickness. These spectra can be analyzed using the parameters in Table 3. Presence of α -Fe could be observed for all the spectra but both its proportion and the degree

of preferred orientation decreased from the film (a) to (d). Both ratio and kind of other components increased with the decrease of single layer thickness. Both spectra for the films (b) and (c) explicitly showed a component with slightly larger hyperfine field than that for α -Fe. There have been reported hyperfine field components larger than that of α -Fe both in γ' -Fe₄N and α'' -Fe₁₆N₂ which have several kinds of iron site. Generally speaking, hyperfine fields at various sites in iron nitrides decrease as a function of the number of interstitial nitrogens⁽⁹⁾. Iron without nearest neighboring nitrogen seems to have the larger hyperfine field in iron nitrides. The similar situation may occur in the films (b) and (c). The spectrum for film (d) is complicated with several kinds of components having smaller hyperfine field than that of α -Fe. It has even the paramagnetic components which had been similarly observed on the zinc blende-type FeNo.₉₁ and its related iron nitride⁽⁷⁾. Relatively higher iron nitrides also seem to be formed at the interface region of the present multilayered Fe/AlN film.

Depth profiles of XPS were measured on the multilayered film (d) [Fe(6.5nm)/AlN(6.2nm)]₃₅ for Fe2p, Al2p, N1s, respectively. The profile for Al changes in-phase with that for N and out-of-phase with that of Fe as shown in the multi-

Fig. 5 Mössbauer spectra for multilayered Fe/AlN films.

Fig. 6 XPS depth profile for multilayered Fe/AlN film (d).

Table 3 ^{57}Fe Mössbauer parameters of multilayered Fe/AlN films

Film	H_{int} (T)	I. S. (mm/s)	Q. S. (mm/s)	Γ (mm/s)	Area (%)
(a)	33.40	-0.029	-0.014	0.39	100
(b)	36.00	-0.004	-0.012	0.55	39
	33.70	-0.002	-0.002	0.37	61
(c)	36.72	-0.014	-0.056	0.64	19
	33.89	-0.002	-0.015	0.42	48
	29.62	0.162	-0.047	1.25	28
	22.22	0.091	-0.094	0.53	5
(d)	33.54	-0.012	-0.014	0.44	17
	27.82	0.109	-0.085	0.92	22
	20.62	0.134	-0.081	1.15	32
	--	0.349	0.682	0.71	23
	--	0.020	--	0.71	5

plots of Fig. 6 except for the oxidized surface region of AlN. Maximum intensities for Al and Fe in the profile correspond to the centers of AlN and Fe layers in thickness, respectively. The former's maximum and minimum are equivalent to the latter's minimum and maximum, respectively. The both spectra for Al and for N shows broadening at around the middle of the depth profile between the respective intensity maximum and minimum, where the measured area corresponds to the interface region between AlN and Fe layers. The broadening of Al peak has double maxima around 74 and 73 eV in binding energy. Binding energies of Al2p about 72.9 eV and 74.0 eV have been reported for aluminum metal and AlN, respectively⁽¹⁰⁾. Aluminum in AlN layer may partly be reduced to metal replaced with Fe. The nitrogen peak broadening also means a presence of more than two kinds of nitrogen at the interface region but can not be assigned at the moment.

In summary, iron metal and AlN were sequentially deposited by rf-sputtering on glass substrates at room temperature. Very anisotropic magnetic behavior and a slight change of coercivity were observed. Formation of iron nitrides at Fe/AlN interface was explicitly observed by He ion yield XAFS and conversion electron Mössbauer spectroscopy. Partial reduction of AlN to aluminum metal at the interface was also observed by XPS depth profile. The observed expansion of Fe lattice parameter can also be understood with the iron nitride formation. This low temperature reaction was most

clearly observed on the multilayered film [Fe(6.5 nm)/AlN(6.2 nm)]₃₆. The present results showed the importance of interface tailoring and characterizations in nanocomposites.

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